

- V. "On Certain Ternary Alloys. Part VI. Alloys containing Aluminium, together with Lead (or Bismuth) and Tin (or Silver)." By C. R. ALDER WRIGHT, D.Sc., F.R.S., Lecturer on Chemistry and Physics in St. Mary's Hospital Medical School. Received May 13, 1892.

The experiments described in the previous five papers\* have shown *inter alia* that when the critical curves are delineated deduced with lead (or bismuth) as heavier immiscible metal, zinc as lighter ditto, and tin (or silver) as "solvent," the curves where bismuth is substituted for lead lie *inside*, and those where silver is substituted for tin *outside*, the original curves; and, further, that in certain cases the formation of definite atomic compounds between particular pairs of metals leads to marked results as regards the mutual relations of the various pairs of conjugate points. Thus, silver and zinc form the compounds  $\text{AgZn}_5$  and  $\text{Ag}_4\text{Zn}_5$ , with the result of producing marked bulging (inwards or outwards) of the curves deduced with these two metals associated with either lead or bismuth. Tin and zinc appear to form the compound  $\text{SnZn}_4$ , with the result of causing a peculiar convergence of the tie-lines when the proportions of metals mixed together permit of the formation of lighter alloys containing tin and zinc in approximately this ratio. Again, the alloys of lead, zinc, and tin are remarkable in that the lower ties slope in one direction, and the upper ones in the opposite direction; and the position where the angle of slope of the lower ties is greatest (which is approximately the point where the excess of tin percentage in the lighter alloy over that in the heavier one is a maximum) is situated very near to that corresponding with a ratio of tin to lead in the heavier alloy denoted by the formula  $\text{SnPb}_3$ .

The following experiments were made with mixtures of metals corresponding with those previously described, excepting that *aluminium* was substituted for *zinc*. One general result appears to be that this substitution always causes the curve to lie *outside* of its former position; and another, that as aluminium does not appear to unite with silver to form compounds analogous to  $\text{AgZn}_5$  and  $\text{Ag}_4\text{Zn}_5$ , the peculiar bulges observed with silver-zinc-lead and silver-zinc-bismuth alloys *are not visible* with silver-aluminium-lead and silver-aluminium-bismuth alloys.

These experiments were commenced about four years ago, at which time moderately pure aluminium was not in the market in any quantity; at least, a number of samples of metals prepared by

\* Part I, 'Roy. Soc. Proc.,' vol. 45, p. 461; Part II, vol. 48, p. 25; Part III, vol. 49, p. 156; Part IV, vol. 49, p. 174; Part V, vol. 50, p. 372.

different makers were examined with the object of obtaining a few pounds of aluminium in the highest practicable state of purity; but, although several of these were stated to contain 98 to 99 per cent. of aluminium and upwards, on analysis far greater amounts of impurity than 1 or 2 per cent. were generally found to be present. Thus, one sample of the so-called pure metal contained upwards of 10 per cent. of iron; another contained, besides some iron, 2·05 per cent. of matters other than silicon and silica insoluble in aqua regia, and 2·91 per cent. of silicon, partly oxidised by aqua regia to soluble silicic acid, partly oxidised but not dissolved, and partly not oxidised at all. The batch finally selected as the best obtainable had the following composition, the sample being drawn from a considerable mass melted together; it was supplied as metal of as nearly perfect purity as commercially possible to obtain, and containing upwards of 99 per cent. of aluminium:—

|                                                            |        |
|------------------------------------------------------------|--------|
| Silicon left undissolved and unoxidised by aqua regia..... | 0·30   |
| Silicon oxidised but not dissolved by aqua regia           | 1·01   |
| „ „ and dissolved by aqua regia..                          | 0·13   |
|                                                            | <hr/>  |
| Total silicon.....                                         | 1·44   |
| Iron.....                                                  | 2·75   |
| Aluminium (by difference) .....                            | 95·81  |
|                                                            | <hr/>  |
|                                                            | 100·00 |

No other impurities of any kind could be detected.\*

When this metal was employed in the production of a compound ternary ingot it was found that almost the whole of the silicon and iron were contained in the lighter alloy in which the aluminium predominated (as compared with the heavier alloy). In some cases, however, when the amount of aluminium in the heavier alloy became

\* [At the present time aluminium containing notably smaller quantities of silicon and iron can be obtained commercially at less than one-eighth the price charged in 1888. Thus a recent sample of ordinary deliveries of "Neuhausen" aluminium was found to contain—

|                                                           |        |
|-----------------------------------------------------------|--------|
| Silicon left undissolved and unoxidised by aqua regia.... | 0·41   |
| Silicon oxidised but not dissolved .....                  | 0·07   |
| „ „ and dissolved by aqua regia.....                      | 0·83   |
|                                                           | <hr/>  |
| Total silicon.....                                        | 1·31   |
| Iron .....                                                | 0·39   |
| Copper .....                                              | 0·07   |
| Aluminium (by difference)....                             | 98·23  |
|                                                           | <hr/>  |
|                                                           | 100·00 |

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considerable, small amounts of iron and silicon were also contained therein.

In some cases, when the amount of aluminium in the upper alloy was large and the other constituents small, the aluminium was taken by difference, the percentages being corrected by means of the above analysis to what they would have been if reckoned on the sum of the aluminium and the other two metals as 100. When, however, the other constituents were present in larger quantity the aluminium was directly determined, the alumina ultimately precipitated being collected and weighed, and the  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$  present therein subsequently determined and subtracted so as to obtain a corrected determination of the aluminium; the percentages were then reckoned on the sum of the aluminium thus found and the other two metals as 100. Thus, for example, an alloy of tin, lead, and aluminium was found to contain 12.01 per cent. of tin and 1.71 per cent. of lead; hence, reckoning the difference, 86.28 per cent., as aluminium, silicon, and iron containing 95.81 per cent. of the first, the corrected analysis is—

|             |                          |       |         |
|-------------|--------------------------|-------|---------|
| Tin.....    | 12.01                    | =     | 12.46   |
| Lead.....   | 1.71                     | =     | 1.77    |
| Aluminium.. | $.86.28 \times 0.9581 =$ | 82.66 | = 85.77 |
|             |                          | <hr/> | <hr/>   |
|             |                          | 96.38 | 100.00  |

On the other hand, an alloy of silver, aluminium, and lead was found to contain the following percentages of these three metals respectively, the aluminium being reckoned from the weight of alumina after subtraction of silica and ferric oxide contained in the mixed precipitate first weighed; whence the annexed composition, calculated on the sum of the three metals as 100:—

|                | Found. | Calculated on sum<br>as 100. |
|----------------|--------|------------------------------|
| Silver.....    | 80.17  | 80.79                        |
| Lead .....     | 6.55   | 6.60                         |
| Aluminium..... | 12.51  | 12.61                        |
|                | <hr/>  | <hr/>                        |
|                | 99.23  | 100.00                       |

In the case of the lighter alloys containing tin, aluminium, and lead (or bismuth) with large percentages of the first metal, it was sometimes found that a notable amount of oxygen was absorbed by the ingot whilst standing molten for eight hours, so that a perceptible deficiency from 100 was observed when all the constituents were added together. With silver-aluminium-lead and silver-aluminium-bismuth alloys this was not the case; on the other hand,

alloys containing antimony instead of tin or silver absorbed oxygen still more readily. In all such cases the analyses are calculated upon the sum of the aluminium, tin, and lead as 100; thus in the following instance:—

|                        | Directly<br>determined. | Calculated on sum<br>as 100. |
|------------------------|-------------------------|------------------------------|
| Tin.....               | 52.53                   | 54.82                        |
| Lead.....              | 8.16                    | 8.52                         |
| Aluminium.....         | 35.12                   | 36.66                        |
| Iron.....              | 0.99                    | —                            |
| Silicon (total).....   | 0.51                    | —                            |
| Oxygen (by difference) | 2.69                    | —                            |
|                        | <hr/> 100.00            | <hr/> 100.00                 |

*Mixtures of Aluminium, Lead, and Tin.*

A number of ternary mixtures were prepared by melting aluminium, and then adding weighed quantities of lead and tin, and stirring vigorously. A considerable amount of scoriæ was usually formed, the lead partially oxidising, and the presence of the lead oxide formed causing the mass to “flour” considerably; usually the molten portion was run off into an ingot mould, and then re-melted, and when in the pasty stage preceding complete fusion rubbed about in the bottom of the crucible with a hot fireclay pestle, so as to promote intermixture. Finally the temperature was raised, so as to bring about complete fusion, and after more vigorous stirring the liquid metal was poured into red-hot narrow clay crucibles or test-tubes, and maintained molten in a lead bath for seven to eight hours in the manner previously described. The temperature during this period of tranquil fusion lay between 750° and 850°, and averaged close upon 800°, as determined by the platinum specific heat pyrometer (Part I). No flux of any kind was used during the previous meltings and stirrings, oxidation being diminished as far as practicable by directing a current of coal gas into the crucible; notwithstanding a much larger amount of oxidation usually took place than with metallic mixtures fused together with potassium cyanide, as in the previous experiments. The metal thus oxidised was usually chiefly *lead*, the tin and aluminium present being comparatively unaffected; the uncertainty as to the amount of lead thus removed in any given case prevented any accurate calculation being made respecting the relative weights of the three metals present in the final compound ingot ultimately obtained; the weight of this was always considerably less than the joint weights of the three metals originally used, partly through oxidation, but principally because the formation of oxide led to a copious amount of

"flouring" of the molten metal, a considerable proportion of the alloys being reduced to minute particles that did not coalesce with the rest of the molten mass, and remained in the crucible when the fused metal was poured into the clay test-tubes. This same flouring action was equally observed when bismuth was substituted for lead; whilst with silver as solvent metal instead of tin it was still more marked; frequently not more than three-quarters or two-thirds of the metals originally weighed up (40 to 50 grammes) were obtained as final compound ingot, and sometimes even less; the deficiency varying according to the success or otherwise of attempts to exclude access of air whilst stirring.

The analysis of the alloys thus prepared was carried out as follows:—A weighed portion was dissolved in hydrochloric acid containing a little nitric acid, and the solution largely diluted. Sulphuretted hydrogen in excess was then passed through, and the solution containing aluminium, &c., filtered off from the precipitated sulphides of tin and lead. These were then separated by sulphide of ammonium, and finally weighed as  $\text{SnO}_2$  and  $\text{PbSO}_4$  in the usual way. The filtrate was saturated with sulphuretted hydrogen, and allowed to stand two or three days to ensure the separation of the last traces of tin; finally ammonia was added, and the precipitate collected, washed, and ignited. The weighed impure alumina was then redissolved by long boiling with hydrochloric acid, any silicic acid present separated by evaporation to dryness, &c., and the iron present estimated volumetrically. It was found impracticable to obtain good results by treating the alloys with nitric acid alone, not only because alloys containing much aluminium are only attacked by that acid with great difficulty, but also because the tin as determined by weighing the undissolved  $\text{SnO}_2$  was over-estimated to an unknown amount on account of the presence of silicon, partly left undissolved as such, partly converted into silicic acid more or less retained by the tin oxide; so that it was necessary to fuse the impure  $\text{SnO}_2$  with sulphur and sodium carbonate to convert into soluble sulphostannate, to precipitate tin sulphide from the filtered aqueous solution by acidulation, and ultimately to roast and weigh as  $\text{SnO}_2$ .\*

The following corrected percentages (reckoned on tin + lead + aluminium = 100) were obtained from the examination of 25 compound ingots representing 50 alloys. In the preparation of these the lead and aluminium were originally weighed up in the proportion of about 2.5 to 1 for the ingots containing smaller amounts of tin; on account of the low density of aluminium this resulted in the formation of approximately equal *volumes* of heavier and lighter alloy

\* With aluminium-bismuth-tin alloys the  $\text{SnO}_2$  undissolved by nitric acid also retains bismuth left behind as sulphide on conversion into sulphostannate and treatment with water (*vide* Part III).

formed in each case. With the mixtures yielding the upper tie-lines, the proportions were altered successively to 1·5 to 1, and, finally, to 1 to 1, as the difference in density between the two alloys formed diminished; so as still to give rise to the formation of the two alloys in approximately equal quantities by volume. It was found that when lead and aluminium (without tin) were fused together, well intermixed, and then allowed to stand molten at about 800° for some hours, the lead retained, on an average, 0·07 per cent. of aluminium dissolved, and the aluminium 1·91 per cent. of lead (mean of nine experiments altogether).

| No. of tie-line. | Heavier alloy. |       |            | Lighter alloy. |       |            | Excess of tin percentage in lighter alloy over that in heavier. |
|------------------|----------------|-------|------------|----------------|-------|------------|-----------------------------------------------------------------|
|                  | Tin.           | Lead. | Aluminium. | Tin.           | Lead. | Aluminium. |                                                                 |
| 0                | 0              | 99·93 | 0·07       | 0              | 1·91  | 98·09      | 0                                                               |
| 1                | 4·60           | 95·33 | 0·07       | 6·25           | 1·86  | 91·89      | + 1·65                                                          |
| 2                | 11·17          | 88·77 | 0·06       | 14·50          | 2·33  | 83·17      | + 3·33                                                          |
| 3                | 12·51          | 87·43 | 0·06       | 20·26          | 2·22  | 77·52      | + 7·75                                                          |
| 4                | 14·01          | 85·75 | 0·24       | 24·50          | 2·55  | 72·95      | + 10·49                                                         |
| 5                | 15·97          | 83·61 | 0·42       | 27·00          | 2·99  | 70·01      | + 11·03                                                         |
| 6                | 18·25          | 81·42 | 0·33       | 27·47          | 2·89  | 69·64      | + 9·22                                                          |
| 7                | 21·13          | 78·40 | 0·47       | 28·98          | 3·39  | 67·63      | + 7·85                                                          |
| 8                | 25·10          | 74·17 | 0·73       | 31·83          | 3·38  | 64·79      | + 6·73                                                          |
| 9                | 33·64          | 65·35 | 1·01       | 39·37          | 5·02  | 55·61      | + 5·73                                                          |
| 10               | 45·41          | 51·89 | 2·70       | 45·34          | 5·58  | 49·08      | — 0·07                                                          |
| 11               | 55·16          | 39·73 | 5·11       | 48·11          | 5·78  | 46·11      | — 7·05                                                          |
| 12               | 61·52          | 29·14 | 9·34       | 52·27          | 7·16  | 40·57      | — 9·25                                                          |
| 13               | 64·21          | 24·52 | 11·27      | 54·62          | 9·38  | 36·00      | — 9·59                                                          |
| 14               | 65·07          | 23·06 | 11·87      | 59·14          | 15·00 | 25·86      | — 5·93                                                          |
| 15               | 63·92          | 21·78 | 14·30      | 60·27          | 17·04 | 22·69      | — 3·65                                                          |

The figures in the last column show that aluminium-tin-lead alloys resemble zinc-tin-alloys in that they furnish a critical curve, the lower ties of which slope to the left (lead side), and the upper ones to the right (zinc or aluminium side). Moreover, the point where the slope of the lower ties is greatest (*i.e.*, practically that where the excess of tin percentage in lighter alloy over that in heavier alloy is a + maximum) is in each case close to that where the ratio of tin and lead contained in the heavier alloy is that represented by the formula  $\text{SnPb}_3$ .

|           | Calculated for $\text{SnPb}_3$ . | $\text{Al,Pb,Sn}$ alloys (5th tie-line). |   | Found.       | $\text{Zn,Pb,Sn}$ alloys. Part V. |
|-----------|----------------------------------|------------------------------------------|---|--------------|-----------------------------------|
| Tin.....  | 15·97                            | 15·97                                    | = | 16·04        | 15·41                             |
| Lead .... | 84·03                            | 83·61                                    | = | 83·96        | 84·59                             |
|           | <hr/> 100·00                     | <hr/> 99·58                              |   | <hr/> 100·00 | <hr/> 100·00                      |

This coincidence would seem to suggest that the peculiar disposition of tie-lines with these two series of alloys (not observed with any others) is due to the tendency towards the formation of the definite compound,  $\text{SnPb}_3$ ; on the other hand, in neither case is any bulge inwards or outwards noticeable in the contour of the critical curve at the part corresponding with this compound, such as is observed in the case of the atomic compounds  $\text{AgZn}_5$  and  $\text{Ag}_4\text{Zn}_5$ .

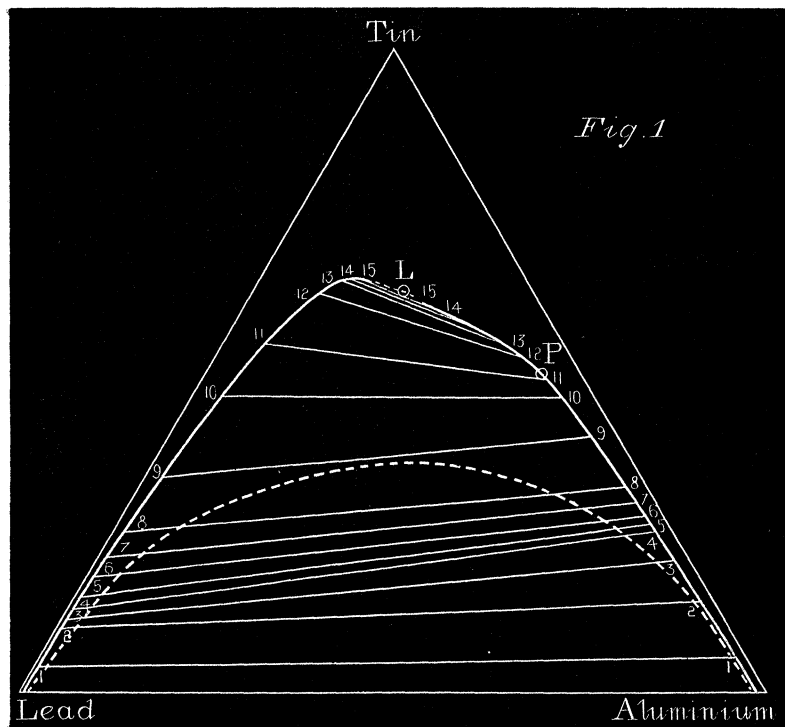


Fig. 1 represents the critical curve plotted from the figures contained in the above table; obviously it lies *outside* the analogous curves obtained at  $650^\circ$  and  $800^\circ$  with zinc-lead-tin alloys (Part V, figs. 4 and 5). The former of these is shown by the inner dotted line. The slopes of the upper ties suggest that there is some tendency towards convergence to a point on the right-hand side; the central point of that part of the curve where this tendency is manifest (marked P in the figure) is that representing the composition tin = 49, lead = 6, aluminium = 45, which is close to that represented by the formula  $\text{SnAl}_4$ , so far as the ratio between tin and aluminium is concerned.

|               | Calculated. | Found.   |             |
|---------------|-------------|----------|-------------|
| Tin.....      | 52.2        | 49       | = 52.1      |
| Aluminium ... | 47.8        | 45       | = 47.9      |
|               | <hr/> 100.0 | <hr/> 94 | <hr/> 100.0 |

An analogous point, more clearly marked, was observed with zinc-lead-tin alloys corresponding with the formula  $\text{SnZn}_4$  (Part V).

On applying the graphical methods of Sir G. G. Stokes for deducing the position of the limiting point L from the above data (Part V), the first method gives the values

$$\begin{aligned} A-B &= 0.6 \\ C+C' &= 125.0 \end{aligned}$$

and the second—

$$\begin{aligned} A+A' &= 39.5 \\ B+B' &= 35.0 \end{aligned}$$

from which the following percentages are deduced:—

|                 | 1st Method. | 2nd Method.  | Mean.       |
|-----------------|-------------|--------------|-------------|
| Lead.....       | 19.0        | 19.75        | 19.4        |
| Aluminium ..... | 18.5        | 17.5         | 18.0        |
| Tin.....        | 62.5        | 62.75        | 62.6        |
|                 | <hr/> 100.0 | <hr/> 100.00 | <hr/> 100.0 |

This mean value represents a ratio of lead to aluminium not far from that indicated by the formula  $\text{PbAl}_7$ .

|                 | Calculated. | Found.     |             |
|-----------------|-------------|------------|-------------|
| Lead .....      | 52.3        | 19.4       | = 51.9      |
| Aluminium ..... | 47.7        | 18.0       | = 48.1      |
|                 | <hr/> 100.0 | <hr/> 37.4 | <hr/> 100.0 |

The corresponding ratio with lead-zinc-tin alloys was nearly that indicated by  $\text{PbZn}_6$ .

#### *Mixtures of Aluminium, Bismuth, and Tin.*

A series of mixtures of aluminium, bismuth, and tin was prepared in just the same way; the analysis of the ternary alloys formed was carried out in precisely the same fashion, excepting that the bismuth sulphide separated from tin sulphide was weighed ultimately as  $\text{Bi}_2\text{O}_3$ ; the results calculated on the sum of aluminium + bismuth + tin = 100 are given in the table below, derived from the examination of 24 compound ingots, representing 48 alloys. As before, the

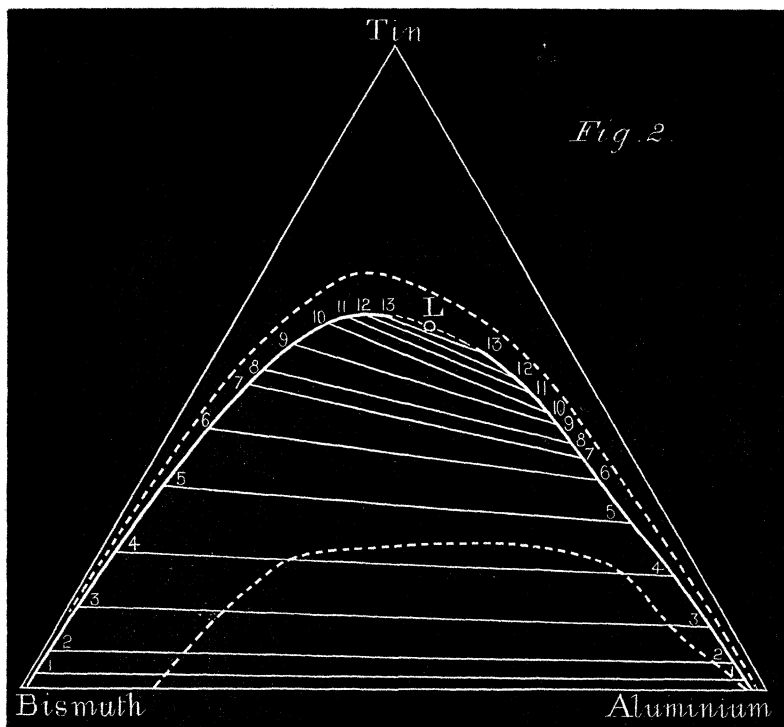
mixtures were kept molten for 7 to 8 hours at a temperature lying between  $750^{\circ}$  and  $850^{\circ}$ , and averaging near  $800^{\circ}$  C.; the earlier ties were obtained with mixtures containing bismuth and aluminium in the ratio by weight of 2.5 to 1, and the later ones in the ratio 1.5 to 1, and, finally, 1 to 1, in such fashion as to effect approximate equality in *volume* of the heavier and lighter alloys formed throughout.

| No. of tie-line. | Heavier alloy. |           |             | Lighter alloy. |           |             | Excess of tin percentage in lighter alloy over that in heavier. |
|------------------|----------------|-----------|-------------|----------------|-----------|-------------|-----------------------------------------------------------------|
|                  | Tin.           | Bis-muth. | Alumin-ium. | Tin.           | Bis-muth. | Alumin-ium. |                                                                 |
| 0                | 0              | 99.72     | 0.28        | 0              | 2.02      | 97.98       | 0                                                               |
| 1                | 2.79           | 96.64     | 0.57        | 2.45           | 2.40      | 95.15       | - 0.34                                                          |
| 2                | 5.57           | 93.58     | 0.85        | 4.90           | 2.75      | 92.35       | - 0.67                                                          |
| 3                | 12.26          | 86.03     | 1.71        | 9.43           | 3.06      | 87.51       | - 2.83                                                          |
| 4                | 21.02          | 76.90     | 2.08        | 17.56          | 3.50      | 78.94       | - 3.46                                                          |
| 5                | 31.37          | 65.19     | 3.44        | 26.40          | 5.27      | 68.33       | - 4.97                                                          |
| 6                | 40.76          | 54.37     | 4.87        | 34.18          | 6.99      | 58.83       | - 6.58                                                          |
| 7                | 46.13          | 47.60     | 6.27        | 35.63          | 8.09      | 56.28       | -10.50                                                          |
| 8                | 50.09          | 41.64     | 8.27        | 38.12          | 8.37      | 53.51       | -11.97                                                          |
| 9                | 54.22          | 35.82     | 9.96        | 42.80          | 9.09      | 48.11       | -11.42                                                          |
| 10               | 56.91          | 30.73     | 12.36       | 42.97          | 9.49      | 47.54       | -13.94                                                          |
| 11               | 57.61          | 27.10     | 15.29       | 45.76          | 9.53      | 44.71       | -11.85                                                          |
| 12               | 58.17          | 24.01     | 17.82       | 49.48          | 13.08     | 37.44       | - 8.69                                                          |
| 13               | 57.23          | 23.20     | 19.57       | 51.32          | 14.37     | 34.31       | - 5.91                                                          |

Fig. 2 represents these values plotted on the triangular system, the outer dotted line being the curve above described for aluminium-lead-tin alloys, obviously lying *outside* the curve obtained with bismuth instead of lead. The inner dotted line represents the corresponding curve with zinc-bismuth-tin (Part V, fig. 7), illustrating the effect of substituting aluminium for zinc.\* With the exception that the one lies outside the other, the aluminium-bismuth-tin and zinc-bismuth-tin curves exhibit a close resemblance, the ties uniformly sloping to the right (*i.e.*, the heavier alloy always containing more tin than the lighter one). No marked bulge inwards or outwards, indicating the formation of an atomic compound, is anywhere perceptible.

The position of the limiting point with zinc-bismuth-tin alloys at  $650^{\circ}$  was deduced (Part V) as yielding a ratio between bismuth and zinc close to that indicated by the formula  $\text{BiZn}_{10}$ ; that similarly

\* The solubility of bismuth in aluminium (without the presence of a third metal) is but little less than that of bismuth in zinc (2.02 per cent. at  $870^{\circ}$  as compared with 2.32 at  $650^{\circ}$  and 2.47 at  $750^{\circ}$ ); but the solubility of aluminium in bismuth is greatly inferior to that of zinc in bismuth (0.28 per cent. at  $870^{\circ}$  as compared with 14.28 per cent. at  $650^{\circ}$  and 15.18 at  $750^{\circ}$ ).



deduced with aluminium-bismuth-tin alloys corresponds with the formula  $\text{BiAl}_{10}$ . Applying Stokes' two methods, large-scale plottings lead to the values  $A-B = -8.2$  and  $C+C' = 111.0$  for the first method, and  $A+A' = 38.0$ ,  $B+B' = 50.0$  for the second method whence the limiting point, L, corresponds to the composition—

|                 | 1st Method. | 2nd Method. | Mean.        |
|-----------------|-------------|-------------|--------------|
| Bismuth.....    | 18.2        | 19.0        | 18.60        |
| Aluminium ..... | 26.3        | 25.0        | 25.65        |
| Tin .....       | 55.5        | 56.0        | 55.75        |
|                 | <hr/> 100.0 | <hr/> 100.0 | <hr/> 100.00 |

|                 | Calculated<br>for $\text{BiAl}_{10}$ . | Found. |             |
|-----------------|----------------------------------------|--------|-------------|
| Bismuth.....    | 43.3                                   | 18.6   | = 42.1      |
| Aluminium ..... | 56.7                                   | 25.65  | = 57.9      |
|                 | <hr/> 100.0                            | 44.25  | <hr/> 100.0 |

*Mixtures of Aluminium, Lead, and Silver.*

The foregoing experiments show that no material alteration is produced in the general characters of the critical curves for alloys containing lead (or bismuth) and zinc as immiscible metals and tin as solvent metal, when aluminium is substituted for zinc, excepting that the curves are raised through the diminished solubility of the two immiscible metals jointly in the solvent. The following experiments show that a similar result follows when silver is substituted for tin as solvent; with the difference that, whereas bulges exist in the lower parts of the critical curves when silver and zinc are simultaneously present, owing to the formation of the definite compounds  $\text{AgZn}_5$  and  $\text{Ag}_4\text{Zn}_5$  (Part V.), no such bulges are noticeable when silver and aluminium are employed; suggesting either that corresponding compounds of silver and aluminium are not formed at all; or that, if they are formed, they are more readily dissociated and broken up on standing molten for seven or eight hours than is the case with the silver-zinc compounds.

A series of mixtures of aluminium, silver, and lead was prepared, precisely as above described (the same aluminium being used), the only difference being that, on account of the higher fusing point of some of the alloys formed, the crucible in which the first fusion and intermixture took place was heated by a small Fletcher's blast gas furnace, instead of a large Bunsen gas burner, provided with a clay jacket and iron chimney, the heat from which, though sufficient for all the mixtures previously described, was not always high enough to permit of the less fusible highly argentiferous alloys being poured into the clay test tubes cleanly, and without partly solidifying in the crucible during the transference. The temperature of the lead bath was similarly increased by using differently arranged burners in such fashion as to maintain a perceptibly higher temperature than any hitherto used, ranging between  $830^\circ$  and upwards of  $900^\circ$ , and averaging about  $870^\circ$  or somewhat higher.

For the lower ties (smaller silver percentages) the lead and aluminium were used in the proportions 2 to 1, so that the volumes of the heavier and lighter alloys formed should not differ widely; for the upper ones increasing proportions of lead were found to be requisite to bring about the same result, so that for the highest ties obtained the lead and aluminium were originally used in the proportion 10 to 1. Owing to oxidation of lead, however, the ratio of the quantities of the two metals present in the compound ingots finally obtained was perceptibly less than this, by an amount too variable to allow an average to be even approximately estimated.

The analysis was made by dissolving in nitric acid and precipitating silver as chloride; the filtrate was evaporated with excess of sulph-

uric acid, and the lead determined as  $\text{PbSO}_4$ ; the filtrate from this was supersaturated with ammonia, and the weight of the impure alumina found corrected for silica and ferric oxide as before, the results being finally calculated on the sum of silver + aluminium + lead as 100.

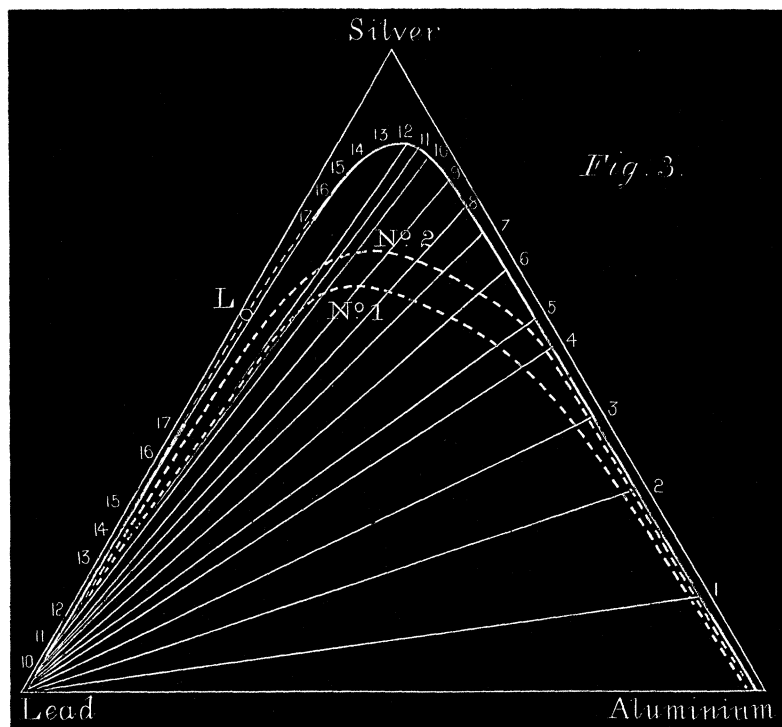
The following table represents the results obtained by the examination of 26 compound ingots forming 52 ternary alloys.

| No. of tie-line. | Heavier alloy. |       |            | Lighter alloy. |       |            | Excess of silver percentage in lighter alloy over that in heavier. |
|------------------|----------------|-------|------------|----------------|-------|------------|--------------------------------------------------------------------|
|                  | Silver.        | Lead. | Aluminium. | Silver.        | Lead. | Aluminium. |                                                                    |
| 0                | 0              | 99.93 | 0.07       | 0              | 1.91  | 98.09      | 0                                                                  |
| 1                | 0.30           | 99.61 | 0.09       | 15.05          | 1.60  | 83.35      | 14.75                                                              |
| 2                | 0.61           | 99.24 | 0.15       | 31.98          | 1.97  | 66.05      | 31.37                                                              |
| 3                | 0.80           | 99.01 | 0.19       | 43.15          | 2.27  | 54.58      | 42.35                                                              |
| 4                | 1.13           | 98.59 | 0.28       | 53.85          | 2.12  | 44.03      | 52.72                                                              |
| 5                | 1.31           | 98.40 | 0.29       | 58.43          | 1.88  | 39.69      | 57.12                                                              |
| 6                | 1.74           | 98.10 | 0.16       | 66.40          | 2.10  | 31.50      | 64.66                                                              |
| 7                | 2.32           | 97.47 | 0.21       | 71.07          | 2.83  | 26.10      | 68.75                                                              |
| 8                | 3.16           | 96.53 | 0.31       | 75.33          | 2.63  | 22.04      | 72.17                                                              |
| 9                | 5.19           | 94.61 | 0.20       | 80.37          | 2.85  | 16.78      | 75.18                                                              |
| 10               | 6.69           | 93.18 | 0.13       | 84.34          | 3.28  | 12.38      | 77.65                                                              |
| 11               | 7.87           | 91.99 | 0.14       | 84.63          | 3.83  | 11.54      | 76.76                                                              |
| 12               | 11.75          | 88.14 | 0.11       | 84.91          | 5.40  | 9.69       | 73.16                                                              |
| 13               | 20.99          | 78.87 | 0.14       | 83.10          | 9.73  | 7.17       | 62.11                                                              |
| 14               | 28.15          | 71.55 | 0.30       | 81.17          | 13.47 | 5.36       | 53.02                                                              |
| 15               | 32.82          | 66.77 | 0.41       | 77.64          | 17.75 | 4.61       | 44.82                                                              |
| 16               | 36.40          | 62.85 | 0.75       | 74.65          | 21.65 | 3.70       | 38.25                                                              |
| 17               | 40.73          | 58.31 | 0.96       | 72.88          | 23.76 | 3.36       | 32.15                                                              |

Fig. 3 represents the critical curve plotted from these values; obviously no marked irregularity of contour is visible, nor any tendency towards convergence of tie-lines to a fixed point, suggesting that aluminium and silver do not form definite atomic compounds analogous to  $\text{Ag}_4\text{Zn}_5$  and  $\text{AgZn}_5$  on the one hand, or to  $\text{AlSn}_4$  on the other. The tie-lines uniformly slope downwards to the left, *i.e.*, the lighter alloy always contains more silver than the heavier one, precisely as in the case of zinc-lead-silver alloys.

The inner dotted curve marked No. 1 represents the curve obtained, as above described, with tin-aluminium-lead alloys, obviously underlying that obtained with silver-aluminium-lead alloys, notwithstanding that the temperature in the latter case was somewhat higher, about  $870^\circ$  as compared with  $800^\circ$ .

The inner dotted curve, marked No. 2, similarly represents the curve obtained with zinc-silver-lead alloys (Part V), omitting the



bulges observed due to the formation of the definite compounds  $\text{AgZn}_5$  and  $\text{Ag}_4\text{Zn}_5$ ; a comparison of this with the aluminium-silver-lead curve shows that the substitution of aluminium for zinc greatly raises the curve, as previously found with aluminium-tin-lead and aluminium-tin-bismuth, as compared with zinc-tin-lead and zinc-tin-bismuth alloys respectively.

On applying Stokes' second method to the above figures, a large-scale plotting leads to the values  $A + A' = 80$ ,  $B + B' = 3.5$  at the limiting point; whence the composition for this point—

|                |                 |   |       |
|----------------|-----------------|---|-------|
| Lead .....     | $\frac{80}{2}$  | = | 40.0  |
| Aluminium..... | $\frac{3.5}{2}$ | = | 1.75  |
| Silver .....   | —               | = | 58.25 |
| <hr/>          |                 |   |       |
| 100.00         |                 |   |       |

representing a ratio between aluminium and lead close to that indicated by the formula  $\text{Pb}_3\text{Al}$ . The corresponding ratio found with aluminium-lead-tin alloys, as above described, was near that indicated

by  $\text{PbAl}_7$ , whilst zinc-lead-silver alloys gave a ratio near that indicated by the formula  $\text{Pb}_2\text{Zn}$  (Part V).

|         | Calculated. | Found.      |             |
|---------|-------------|-------------|-------------|
| Pb..... | 95·8        | 40·0        | = 95·8      |
| Al..... | 4·2         | 1·75        | = 4·2       |
|         | <hr/> 100·0 | <hr/> 41·75 | <hr/> 100·0 |

*Mixtures of Aluminium, Bismuth, and Silver.*

A series of mixtures of aluminium, bismuth, and silver was prepared in precisely the same way, the temperature during the period of tranquil fusion being the same, viz., between  $830^\circ$  and upwards of  $900^\circ$ , averaging about  $870^\circ$ , or a little higher; for the lower ties, as before, bismuth and aluminium were employed in about the relative proportion 2 to 1, increasing quantities of bismuth being used for the upper ones, until the proportion reached about 10 to 1. The alloys were analysed by dissolving in nitric acid, and precipitating the silver as chloride, and diluting the filtrate and precipitating with sulphuretted hydrogen; the sulphide of bismuth was ultimately weighed as oxide, after dissolving in nitric acid and precipitating with ammonium carbonate; whilst the aluminium was precipitated from the sulphuretted hydrogen filtrate by ammonia, and the weighed alumina corrected for silica and ferric oxide, as before; the results being in all cases calculated upon the sum of silver, bismuth, and aluminium found as 100.

The following table represents the results obtained by the examination of 20 compound ingots, representing 40 alloys:—

| No. of tie-line. | Heavier alloy. |          |            | Lighter alloy. |          |            | Excess of silver percentage in lighter alloy over that in heavier. |
|------------------|----------------|----------|------------|----------------|----------|------------|--------------------------------------------------------------------|
|                  | Silver.        | Bismuth. | Aluminium. | Silver.        | Bismuth. | Aluminium. |                                                                    |
| 0                | 0              | 99·72    | 0·28       | 0              | 2·02     | 97·98      | 0                                                                  |
| 1                | 0·74           | 98·39    | 0·87       | 12·30          | 2·66     | 85·04      | 11·56                                                              |
| 2                | 1·59           | 97·43    | 0·98       | 24·20          | 3·49     | 72·31      | 22·61                                                              |
| 3                | 1·95           | 97·31    | 0·74       | 33·95          | 3·50     | 62·55      | 32·00                                                              |
| 4                | 2·01           | 97·49    | 0·50       | 51·80          | 3·39     | 44·81      | 49·79                                                              |
| 5                | 4·81           | 94·72    | 0·47       | 68·63          | 3·94     | 27·43      | 63·82                                                              |
| 6                | 11·51          | 88·09    | 0·40       | 81·29          | 4·71     | 14·00      | 69·78                                                              |
| 7                | 21·56          | 77·72    | 0·72       | 83·75          | 6·45     | 9·80       | 62·19                                                              |
| 8                | 25·41          | 74·07    | 0·52       | 83·88          | 7·98     | 8·14       | 58·47                                                              |
| 9                | 31·05          | 68·28    | 0·67       | 82·60          | 9·96     | 7·44       | 51·55                                                              |
| 10               | 40·92          | 57·97    | 1·11       | 75·64          | 18·70    | 5·66       | 34·72                                                              |
| 11               | 48·53          | 49·62    | 1·85       | 68·16          | 28·50    | 3·34       | 19·63                                                              |

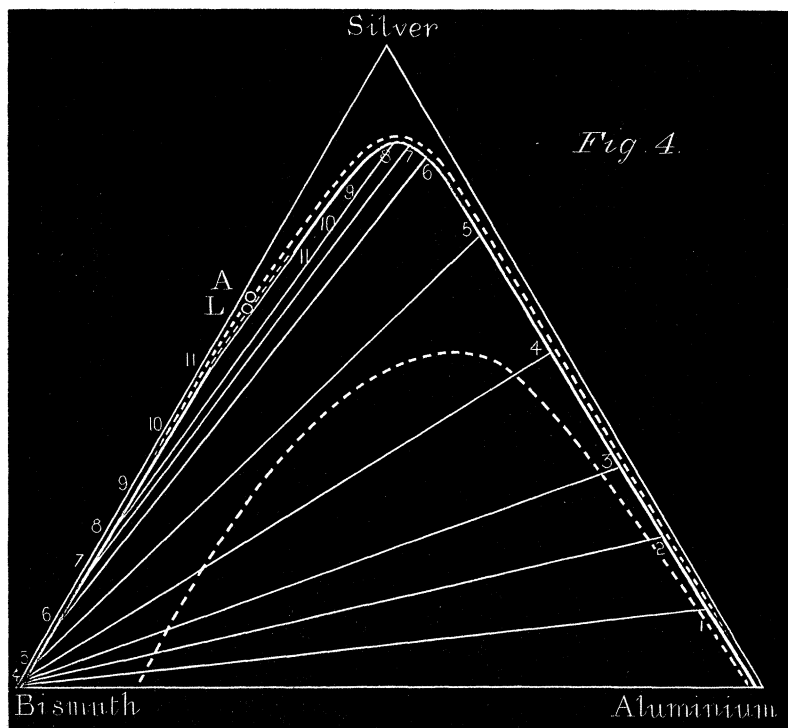


Fig. 4 represents the critical curve deduced from these values; the point marked A represents a mixture of metals that did not separate into two ("real" alloy, containing  $\text{Ag} = 59.9$ ,  $\text{Bi} = 37.3$ ,  $\text{Al} = 2.8$ ).

The outer dotted line is the corresponding curve, obtained as above described, with aluminium-lead-silver alloys, distinctly illustrating the raising of the curve brought about by the substitution of lead for bismuth with aluminium and silver, just as previously found for zinc and tin, zinc and silver, and aluminium and tin.

The inner dotted curve is that obtained with zinc-bismuth-silver alloys (Part V), omitting the bulges, illustrating the effect of substituting aluminium for zinc in raising the curve, just as in the previous cases with lead and tin, bismuth and tin, and lead and silver.

Obviously no marked irregularity of contour is noticeable, nor any change of direction of tie-lines, nor any tendency to converge to a point, apparently indicating the absence of any tendency of aluminium to form definite compounds with silver, like those formed by zinc with silver or tin.

All the tie-lines slope to the *left*, just as in the case of the other

silver-containing ternary alloys examined (silver-lead-zinc, silver-bismuth-zinc, and silver-aluminium-lead), *i.e.*, the lighter alloy always contains the most silver. With tin as solvent metal, on the other hand, the upper tie-lines always slope to the *right*, *i.e.*, the heavier alloy contains the most tin; with bismuth-zinc-tin and bismuth-aluminium-tin alloys this direction of slope is observed with all the tie-lines; but with lead-zinc-tin and lead-aluminium-tin the lower ties slope to the left, apparently because of the formation of definite compounds  $\text{SnZn}_4$  and  $\text{SnAl}_4$  on the one hand, and  $\text{SnPb}_3$  on the other, the influence of the former of which on the bismuth-containing alloys is not perceptible, on account of the lower situation of the curve.

On applying Stokes' second system to the above figures, a large-scale plotting leads to the values at the limiting point  $A + A' = 79$ ,  $B + B' = 4\cdot5$ ; whence the composition

|                |                     |   |              |
|----------------|---------------------|---|--------------|
| Bismuth .....  | $\frac{79}{2}$      | = | 39·50        |
| Aluminium..... | $\frac{4\cdot5}{2}$ | = | 2·25         |
| Silver .....   | —                   | = | 58·25        |
|                |                     |   | <hr/> 100·00 |

representing a ratio between bismuth and aluminium near to that indicated by the formula  $\text{Bi}_2\text{Al}$ .

|         | Calculated. | Found.      |             |
|---------|-------------|-------------|-------------|
| Bi..... | 93·9        | 39·50       | = 94·6      |
| Al..... | 6·1         | 2·25        | = 5·4       |
|         | <hr/> 100·0 | <hr/> 41·75 | <hr/> 100·0 |

The corresponding ratio found previously in the case of bismuth-zinc-silver alloys was near that indicated by the formula  $\text{BiZn}_2$  (Part V); whence it would seem that, although the composition of the alloys corresponding with certain points on the analogous curves obtained where aluminium is substituted for zinc exhibit some degree of parallelism (*e.g.*, those corresponding with the ratios  $\text{SnZn}_4$  and  $\text{SnAl}_4$ ), yet this does not apply to the composition represented by the limiting points; and, further, the composition at the limiting point corresponds with a ratio between the two immiscible metals which varies in each case with the nature of the solvent metal. Thus in the eight cases hitherto investigated the ratios approximately found are as follows:—

| Immiscible metals.         | Solvent metal. | Approximate ratio.       |
|----------------------------|----------------|--------------------------|
| Lead and zinc . . . . .    | Tin            | $\text{PbZn}_6$          |
| " " . . . . .              | Silver         | $\text{Pb}_2\text{Zn}$   |
| Lead and aluminium . . .   | Tin            | $\text{Pb}_2\text{Al}_7$ |
| " " . . . . .              | Silver         | $\text{Pb}_3\text{Al}$   |
| Bismuth and zinc . . . . . | Tin            | $\text{BiZn}_{10}$       |
| " " . . . . .              | Silver         | $\text{BiZn}_2$          |
| Bismuth and aluminium . .  | Tin            | $\text{BiAl}_{10}$       |
| " " . . . . .              | Silver         | $\text{Bi}_2\text{Al}$   |

The author has much pleasure in acknowledging the assistance of Mr. Sydney Joyce in carrying out a large proportion of the analytical work requisite for the experiments above described.

VI. "The Conditions of the Formation and Decomposition of Nitrous Acid." By V. H. VELEY, M.A., University Museum, Oxford. Communicated by Professor ODLING, F.R.S. Received April 12, 1892.

#### *Introductory.*

Throughout the whole science of chemistry there is possibly no reagent so frequently represented as taking part in various transformations, but of which so little definite is known, as nitrous acid. In many text-books its properties are cursorily discussed in a few lines, while some writers have gone so far as to deny its existence altogether even in the presence of nitric acid. Among the commoner examples of reactions considered to be effected by nitrous acid, it is necessary only to mention the conversion of the primary paraffinoid amines into the corresponding alcohols, the formation of nitroso- and diazo-derivatives, and the preparation of the fulminates. In a previous paper\* it was my endeavour to prove that the solution of certain metals in nitric acid was conditioned by the presence of nitrous acid, and the cause of the chemical change explained on the supposition that the acid is alternately formed and decomposed.

As a fitting corollary to these investigations, it seemed worthy of interest to examine to some extent the validity of this hypothesis by endeavouring to imitate the reactions supposed to take place on solution of the metal, either when no metal is present, or when the metallic salt is either present or absent.

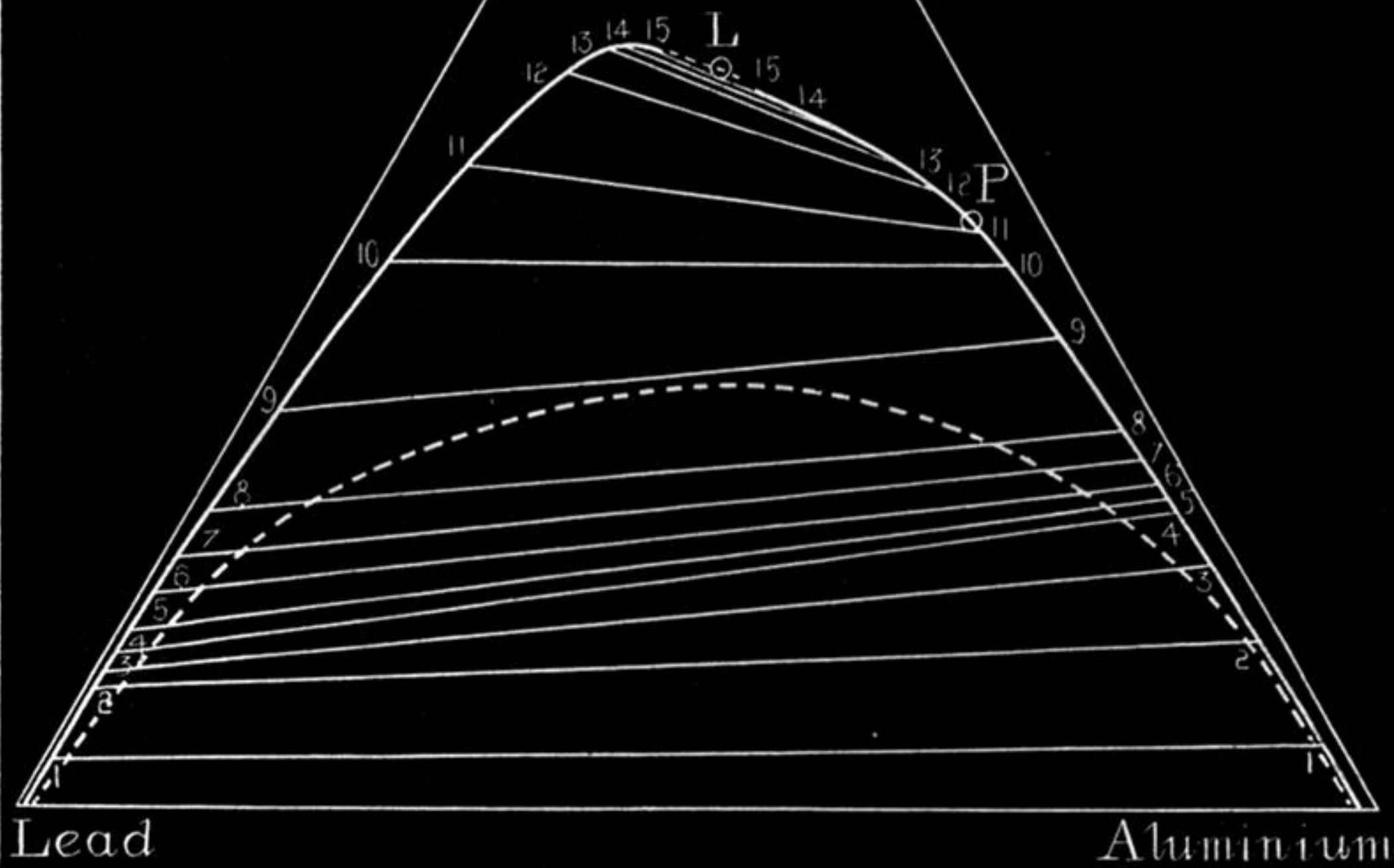
The stability of nitrous acid in presence of nitric acid forms also a part of this research, and, conversely, the stability of nitric acid in absence of nitrous acid is discussed.

In the present, as in my former, investigations, it will be under-

\* 'Phil. Trans.,' 1891, A, pp. 312—313.

Tin

*Fig. 1*



Tin

*Fig. 2.*

